Structural and Physical Properties of Diluted Magnetic Semiconductor Ga1-xCrxN(希薄磁性半導体Ga1-xCrxNの構造と物性に関する研究)

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論文内容要旨

Diluted magnetic semiconductors (DMS) have been of great interest in terms of application to spintronic devices which combine semiconductor and magnetism. GaN doped with transition metal ions have attracted much attention because it is predicted theoretically that they have a high Curie temperature (T_c) above room temperature (RT). Many experimental researches have been focused on GaMnN. However, the magnetism of GaMnN is very controversial and confusing due to the presence of secondary phases. On the other hand, most of experimental researches on GaCrN report ferromagnetism above RT. However, most of the previous researches on GaCrN relied on crystallographic results such as X-ray diffraction (XRD) and magnetic measurements using superconducting quantum interference device (SQUID) for judging ferromagnetism, although XRD is too poor to detect magnetic precipitations, while SQUID is so sensitive to be disturbed by ferromagnetic precipitations. Very recently, magnetic circular dichroism (MCD) study of GaCrN has shown that the intrinsic magnetism of GaCrN is paramagnetic. Although many of experimental researches on GaCrN indicate ferromagnetism, the intrinsic magnetism of GaCrN still remains as an open question. More detailed and systematic studies from microscopic viewpoints including MCD, X-ray absorption fine structure (XAFS), X-ray photoemission spectroscopy (XPS) are needed before exploring applications using this material.

In this research, the structural, magnetic, and electronic structural properties of GaCrN with wide range of Cr composition have been investigated. The successful growth of $Ga_{1-x}Cr_xN$ films with high Cr content using NH_3-MBE was investigated by using XRD measurements. In wide range 2θ–ω scan results using an open detector, it has been observed that for Cr content above 20 at.% in $Ga_{1-x}Cr_xN$ phase separation of cubic CrN occurs. In the high resolution 2θ–ω scan results, using an analyzer detector, clear lattice constant variation has been observed. The *c*-axis lattice constant systematically decreases with the increasing Cr concentration. On the other hand, the lattice constants of the *ab*-plane are pinned on the fully relaxed GaN buffer layer due to coherent growth on it. As a result, it has been confirmed that the lattice constant of GaCrN is smaller than that of GaN and 300nm thick $Ga_{1-x}Cr_xN$ layer receives two dimensional tensile strain up to Cr= 10.1 at.% on a GaN buffer layer. Based on the results of the systematic lattice constant variation and no indication of any other secondary phases up to Cr=10.1 at.%, we can conclude that the $Ga_{1-x}Cr_xN$

films have a wurtzite structure with Cr substituting for the Ga site without forming a secondary phase at least up to a Cr content of 10.1 at.%, within the detection limit of the XRD measurements.

Magnetic properties of the structurally well-defined $Ga_{1-x}Cr_xN$ have been investigated by SQUID magnetometer. The films show ferromagnetic behavior up to 300K and the ferromagnetic behavior is consistent with most of the previous reports on Cr-doped GaN. The present research has also observed a coexisting paramagnetic component with the ferromagnetic component in Cr-doped GaN. However, since the remanent magnetic moment anomalously increases at the low temperature range and the magnetization as a function of magnetic field and temperature curves include this anomaly, the magnetic properties cannot be understood by a simple coexistence of ferromagnetic and paramagnetic components. Total effective magnetic moment and spontaneous magnetic moment per Cr atom decrease with the increasing Cr concentration. Considering Cr^{3+}=3 μ_B/atom, the Cr atoms in $Ga_{0.987}Cr_{0.013}N$ are almost all magnetically activated but those in the $Ga_{0.937}Cr_{0.063}N$ and $Ga_{0.899}Cr_{0.101}N$ are only about 35% and 26% activated, respectively, at a high magnetic field of 7 T at 1.7K. Spontaneous magnetic moments estimated at 7T and 300K are a mere 12~15% of the total effect magnetic moments. These results indicate very small ferromagnetic contributions in $Ga_{1-x}Cr_xN$.

It is confirmed that *s*, *p-d* exchange interactions in $Ga_{0.97}Cr_{0.03}N$ and the magnetic field dependence of the peak intensity of MCD show paramagnetic behavior in optical MCD experiments. The ferromagnetic component observed by SQUID magnetization measurement could not be detected by the MCD experiment. This indicates that there is an unidentified ferromagnetic material, which has a different electronic structure from $Ga_{1-x}Cr_xN$. These results are consistent with a previous report on metal-organic MBE grown Cr-doped GaN.

In this thesis, for the first time, a clear Cr $L_{2,3}$-edge XMCD spectra of Cr-doped GaN has been observed clearly at low temperature. In the sample of $Ga_{0.97}Cr_{0.03}N$, the temperature dependence of the XMCD peak intensity was well described by the Curie-Weiss law, and the Weiss temperature was estimated as 14 K. Based on a recent calculation showing a low T_c in GaMnN, the anomalous remanent moment at low temperature in SQUID, and the estimated 14K Weiss temperature, it is possible that another magnetic component, which has a very low T_c, also contributed to the magnetism of $Ga_{1-x}Cr_xN$. The macroscopic magnetic characteristic measured by SQUID magnetometer showed the ferromagnetic behavior as an offset magnetization coexisting with the paramagnetic component in the $Ga_{0.97}Cr_{0.03}N$ film over the entire temperature range from 1.7K to 300K. However, the ferromagnetic component was not detected in the XMCD measurement in the temperature range from 40K to 300K.

Some limited part in the $Ga_{1-x}Cr_xN$ films such as the interface of the $Ga_{1-x}Cr_xN$ epilayer and GaN buffer layer was considered as a possible origin of the observed ferromagnetism in SQUID. However, the systematic thickness dependence on magnetization means that the ferromagnetic component does not exist in a limited part in the film but is distributed over the entire bulk. Contributions of other magnetic impurity like Fe are also unlikely because of usage of high purity Cr source during MBE growth. Cr clusters do not adequately explain the observed ferromagnetism in SQUID measurements.

Consequently, the intrinsic magnetic property of $Ga_{1-x}Cr_xN$ is paramagnetic and the origin of the observed ferromagnetism in the SQUID measurements is an unidentified ferromagnetic phase, which is most likely related to Cr.

Also, for the first time, the local structure around Cr atoms in paramagnetic $Ga_{1-x}Cr_xN$ with an unidentified Cr related ferromagnetic component has been investigated by using X-ray absorption spectroscopy technique. In the Cr K-edge extended X-ray absorption fine structure analysis, it is confirmed that the local structure around Cr atoms maintains tetrahedral symmetry up to Cr=10.1 at.% like the local symmetry of the ideal wurtzite GaN and Cr atoms in all three samples have most likely substituted for the Ga sites in GaN. It is also confirmed that the second nearest neighbors (SNNs) of Cr in the sample with x=0.013 consist of only 12 Ga atoms and that of the sample with x=0.063 consist of Ga and Cr atoms at about Ga:Cr = 2:1. This result indicates the Cr atoms are isolated for x=0.013 and the unexpectedly high existence of Cr-N-Cr networks for x=0.063. The intrinsic magnetic property of $Ga_{1-x}Cr_xN$ is paramagnetic. Since the Cr atoms for x=0.013 are isolated in $Ga_{1-x}Cr_xN$, the paramagnetism is reasonable. It is also confirmed that the total effective magnetic moment per Cr atom decreased with increasing Cr concentration. It is known that the exchange interactions of Cr-Cr in Cr metal and Cr-N-Cr in CrN are antiferromagnetic. Based on the correlation between the assembled Cr atoms and the weak magnetic moment for x=0.063 compared with x=0.013, it is suggested that the Cr-N-Cr networks should play an important role in the decreased magnetic momentum in $Ga_{1-x}Cr_xN$ with high Cr content through the antiferromagnetic interaction of the Cr-N-Cr networks. In Cr K-edge X-ray near edge absorption structure analysis, it is confirmed that the oxidation states of Cr ion in $Ga_{1-x}Cr_xN$s are closed to 3+ by comparing with some other Cr containing materials, whose oxidation state is clearly defined. In addition, the oxidation state of Cr ion in $Ga_{1-x}Cr_xN$ slightly increases with increasing Cr concentration. Estimated oxidation states of $Ga_{1-x}Cr_xN$ samples are 3.3+ for x=0.013, 3.6+ for x=0.063, and 3.6+ for x=0.101 based on the linear dependence between the energy positions of the Cr K-edge in the reference samples and the oxidation state of chromium.

Through this local structural investigation, we could not get any other local structural information which could distinguish the major paramagnetic $Ga_{1-x}Cr_xN$ phase from the unidentified ferromagnetic phase.

Finally, for the first time, the electronic structure of $Ga_{1-x}Cr_xN$ has been investigated by using bulk sensitive hard X-ray photoemission spectroscopy excited by synchrotron radiation. Cr-doping induces a systematic energy shift to the low binding energy side in core level and valence band spectra. This means the E_F shift is caused by the formation of localized Cr 3*d* bands in the band gap, which trap electrons thus result in a low electron concentration in the conduction band. Cr-doping introduces a new electronic level in the band gap and causes some change in the valence band structure. Based on the atomic subshell photoionization cross section at this high excitation energy, the new electronic state and modified valence structure are considered to dominantly Ga 4*s* originated states. In the core level study, we have not only observed the chemical shift in N 1*s* core level spectra but also that in the second neighbor Ga via the formation of Cr-N bonds by Cr-doping. These results are evidence that the Ga valence electrons are strongly affected by the second nearest neighbor Cr atoms through Cr 3*d*-Ga 4*s* hybridization.

In this thesis, the structure, magnetic properties, and electronic structure of Cr-doped GaN have been investigated by using various experimental methods including synchrotron radiation experiments. Also, some correlations between the physical properties have been discussed. Putting all experimental results in this study together, the present $Ga_{1-x}Cr_xN$ is paramagnetic DMS and an unidentified ferromagnetic phase contributes to the observed RT ferromagnetism in SQUID magnetization measurements.

In conclusion, the present studies reveal that the intrinsic magnetism of the GaCrN is paramagnetic and the ferromagnetic behavior observed by SQUID is attributed to an unidentified ferromagnetic impurity which is undetectable even by the present advanced diagnosis.

論文審査結果の要旨

最近、理論的に実験的に室温で強磁性を示す可能性が高い磁性半導体として遷移金属イオンを添加した GaN 系が注目されている。しかし、そのような強磁性が本質的な磁性ではなく、結晶中に析出されている不純物がその強磁性の原因になるという報告もあり、これらの系に関する本質的な磁性は未だ解明されていない。これらの系に関する本質的な磁性を解明するためには、磁性原子が母体に添加されたときに母体の構造及び物性がどのような影響を受けるかを系統的に調べる必要がある。本論文の目的は、分子線エピタキシー(MBE)法を用いて単原子層レベルで成長制御した Cr ドープ GaN 薄膜を作製し、結晶構造、Cr 周囲の局所構造、磁性、電子構造を系統的に研究し、その構造と物性の相関を明らかにすることである。

本論文は全7章より構成されている。

第1章は序論であり、研究背景とともに従来の研究を紹介し、その中での本研究の位置づけを述べ、本研究の目的を設定した。

第2章は本研究で用いた実験技術の原理と実験装置の詳細に関する。

第3章は GaCrN の MBE 成長とその結晶評価に関する。すなわち、本研究では Cr 濃度を系統的に変化した高品質 GaCrN 薄膜を MBE 法により成長させ、Cr 不純物ならびに CrN 等の2次相の析出が無いことが確認された Cr ドープ GaN 薄膜に対してその局所構造解析ならびに磁性、電子物性評価研究の試料として採用した。

第4章は GaCrN 薄膜の磁性に関する。磁性評価は SQUID 磁速計及び磁気円二色性 (MCD) を用いて行った。SQUID による磁化の磁場依存性及び温度依存性の結果から $Ga_{1-x}Cr_xN$ は常磁性と室温以上のキュリー点を持つ強磁性が共存していることがわかった。しかし、残留磁化の温度依存性には低温で磁化が急に増加する現象が観測され、単純な常磁性と強磁性の共存ではないことがわかった。Cr 濃度が 1.3% 以下の低濃度試料では磁気モーメントが Cr^{3+}に対応する磁気モーメントを持つのに対して、6.3%及び 10.1%の試料は磁気モーメントが減少した。さらに Cr ドープ GaN の本質的な磁性を調べるために光学吸収を用いた MCD 実検及び Cr の軟 X 線吸収を用いた MCD 実検(XMCD)を行った。その結果、MCD 実験で常磁性は確認できたが SQUID で観測した強磁性的は観測できなかった。この結果から GaCrN は本質的に常磁性を持つ希薄磁性半導体で SQUID で観測した強磁性成分は非常に微小な Cr 化合物相によるものと結論した。

第5章は GaCrN 薄膜中の Cr 周囲の局所構造解析に関する。Cr K-edge EXAFS 法により GaCrN 中の Cr 周囲の局所構造を調べた。その結果、Cr 濃度の増加とともに第二隣接原子位置に Cr が集まり Cr-N-Cr ネットワークを形成していることがわかった。この EXAFS 結果と SQUID 結果の磁気モーメントの濃度依存性との比較から Cr 高濃度試料の磁気モーメント減少は Cr-N-Cr のネットワークに起因する反強磁性的な相互作用によると議論した。

第6章は GaCrN 薄膜の電子状態に関する。高エネルギー光電子分光を用いて GaCrN のバルク電子構造を調べ、Cr ドープによってバンドギャップ内に状態が出現した。この結果は Cr*3d* 軌道と Ga4*s* 軌道とが N 原子を介在して混成し、ギャップ内に新たな状態が出現しことを示唆している。

第7章は結論であり、本研究を総括している。

以上要するに、本論文は GaCrN の構造と磁性と電子状態の相関を明らかにしたものであり、応用物理学、結晶工学、磁気材料工学に資すること大であると認められる。

よって，本論文は博士(工学)の学位論文として合格と認める。